

# Experimental and Modeling Studies for a Reactive Batch Distillation Column

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**Abstract:** Modeling of esterification reaction of ethanol with acetic acid in a reactive batch distillation column is investigated. The dynamic model developed is verified using the data of a theoretical study available in the literature. However, the existing models are found to be inappropriate for this system when compared with the experimental data. Then the model is improved using the data obtained from the experiments performed on a lab-scale column. In the model, different rate expressions and different thermodynamic models ( $\phi-\phi$ , EOS- $G_{ex}$ , and  $\gamma-\phi$  methods) considering different equations of state (EOS), mixing rules and activity coefficient models are used. It is found that the  $\gamma-\phi$  approach considering van der Waals mixing rule and NRTL activity coefficient model gives the best fit between the dynamic model and the results of the experiments for the system under study.

**Keywords:** Reactive Distillation, Batch Column, Mathematical Modeling, Dynamic Simulation, Ethyl Acetate Production.

## 1. INTRODUCTION

Reactive distillation, which is combination of reaction and separation operations in a single unit, has many advantages over conventional processes. Modeling of this process is a challenging task due to its complex dynamics, highly nonlinear behaviour, complex interactions between vapor-liquid equilibrium (VLE) and chemical kinetics.

The system studied in this work is an esterification reaction where ethanol (EtOH) reacts with acetic acid (AcAc) to produce ethyl acetate (EtAc) and water (H<sub>2</sub>O). In this quaternary system, azeotropes are formed between EtOH-H<sub>2</sub>O, EtAc-H<sub>2</sub>O, EtAc-EtOH, and EtAc-H<sub>2</sub>O-EtOH. In the literature, most of the studies on this reaction utilized the numerical methods of solution (Chang and Seader, 1988; Bogacki et al., 1989; Simandl and Svrcek, 1991) and some others worked on its thermodynamics for phase equilibrium (Okur and Bayramoglu, 2001; Park et al., 2006) with very simple models in simulation. Assumptions considered are; ideal plates with constant molar holdup, negligible tray hydrodynamics and steady state condition. Alejski and Duprat (1996) dealt with the dynamic simulation of a reactive distillation column for EtAc system in presence of a catalyst. Tang et al. (2003) showed that, NRTL activity coefficient model parameters predict the VLE data of this system well. Both of these dynamic studies are done on continuous column. On the other hand, unlike continuous columns very few studies are done for modeling of reactive batch columns. Mujtaba and Macchietto (1997) developed an optimization algorithm and Monroy-Loperena and Alvarez-Ramirez (2000) developed an output-feedback control algorithm for a reactive batch column. However, in their studies they used very simplified VLE models and the model is not checked with experimental data.

The objective of this study is to develop a dynamic mathematical model for the esterification reaction of EtOH and AcAc in a reactive batch distillation column (RBDC) by verifying it with experimental data. Thus, different thermodynamic models are used for VLE calculations in order to obtain a good fit with the experimental data.

## 2. EXPERIMENTAL

The batch distillation column (Fig. 1) used in this study (Bahar, 2007) has an inner diameter of 5 cm, a height of 40 cm, and 8 sieve plates. The overall column parameters and experimental operating conditions are given in Table 1. The column is first operated at total reflux. After steady state is reached, reflux ratio is set to a predefined value. Analyses of the collected samples are done through Gas Chromatography.

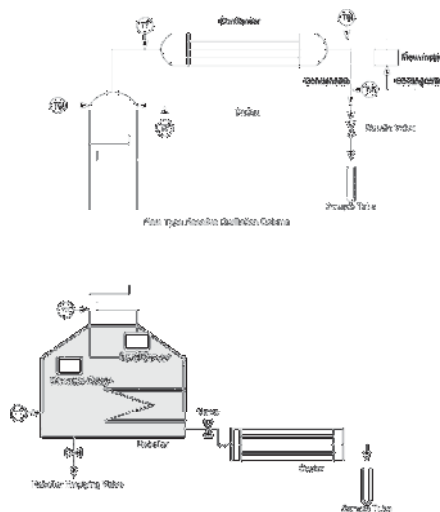


Fig. 1. Reactive Batch Distillation Column.

**Table 1. Experimental Column Parameters and Operating Conditions**

Total fresh feed, mol	311.67
Feed composition (EtAc, EtOH, H <sub>2</sub> O, AcAc), mole fraction	0.0, 0.5, 0.0, 0.5
Column holdup, mol	
condenser+drum	30
internal plates	0.779
Reboiler heat duty, J/h	2.016x10 <sup>6</sup>
Column pressure, bar	1.013
Cooling water flow rate, lt/min	1.0

### 3. RBDC MODELING

The unsteady state model of RBDC is based on model of Yıldız et al. (2005). The assumptions employed are negligible vapour holdup, constant volume of tray liquid holdup, constant liquid molar holdup in the reflux drum, total condenser, negligible fluid dynamic lags, linear pressure drop profile, Murphree tray efficiency, approximated enthalpy derivatives and adiabatic operation. The balance equations for column reboiler, trays and reflux-drum-condenser system are given as follows:

Reboiler:  $j = 1, \dots, NC$

$$dM_1 / dt = L_2 - V_1 \quad (1)$$

$$d(M_1 x_{1j}) / dt = L_2 x_{2j} - V_1 y_{1j} + \epsilon_j R_1 M_1 \quad (2)$$

$$d(M_1 h_1) / dt = L_2 h_2 - V_1 H_1 + Q_1 \quad (3)$$

where the reboiler holdup,  $M_1$ , is as given in (4) where  $M_f^0$  is the molar amount of feed initially charged to the column.

$$M_1 = M_f^0 - \sum_{n=2}^{NT+2} M_n - \int_0^t D(\tau) d\tau \quad (4)$$

Trays:  $i = 2, \dots, N_{T+1}$ ;  $j = 1, \dots, NC$

$$dM_i / dt = L_{i+1} + V_{i-1} - L_i - V_i \quad (5)$$

$$d(M_i x_{ij}) / dt = L_{i+1} x_{i+1,j} + V_{i-1} y_{i-1,j} - L_i x_{ij} - V_i y_{ij} + \epsilon_j R_i M_i \quad (6)$$

$$d(M_i h_i) / dt = L_{i+1} h_{i+1} + V_{i-1} H_{i-1} - L_i h_i - V_i H_i \quad (7)$$

where  $M_i = (\rho_i^{avg} / Mw_i^{avg}) v_i$  is the molar holdups on trays where  $\rho_i^{avg}$  is the average density of the mixture on the  $i^{\text{th}}$  tray,  $Mw_i^{avg}$  is the average molecular weight of the mixture on the  $i^{\text{th}}$  tray,  $v_i$  is the volume of the liquid tray holdup.

Reflux-drum-condenser system:  $j = 1, \dots, NC$

$$dM_{NT+2} / dt = V_{NT+1} - L_{NT+2} - D \quad (8)$$

$$\frac{d(M_{NT+2} x_{NT+2,j})}{dt} = V_{NT+1} y_{NT+1,j} - L_{NT+2} x_{NT+2,j} - D x_{NT+2,j} + \epsilon_j R_{NT+2} M_{NT+2} \quad (9)$$

$$\frac{d(M_{NT+2} h_{NT+2})}{dt} = V_{NT+1} H_{NT+2} - L_{NT+2} h_{NT+2} - D h_{NT+2} - Q_{NT+2} \quad (10)$$

where  $R_i$  is the reaction rate at  $i^{\text{th}}$  stage in mol/h and can be expressed as given in (11) and the rate expression,  $r_i$ , without catalyst is expressed as  $r = k_1 x_2 x_4 - k_2 x_3 x_1$ . The forward and backward reaction rate constants in lt/gmol.min are

$k_1 = 29100 \exp(-7190/T(K))$  and  $k_2 = 7380 \exp(-7190/T(K))$ , respectively (Alejski and Duprat, 1996).

$$R_i = r_i \rho_i / MW_i \quad \text{for } i = 1, \dots, N_{T+2} \quad (11)$$

The reflux ratio is defined as  $R = L_{NT+2} / D$ . The subscripts  $i$  and  $j$  are for stage and component numbers, respectively.  $i=1$  for reboiler,  $i=2, \dots, N_{T+1}$  for trays and  $i=N_{T+2}$  for reflux-drum-condenser unit. The components are numbered in the subscripts as follows: EtAc-1, EtOH-2, H<sub>2</sub>O-3, and AcAc-4.

In energy balance equations, no additional term for the heat of reaction is included because, the enthalpies are referred to their elemental state for which the heat of reaction is accounted automatically and thus, no separate term is needed (Mujtaba and Macchietto, 1997). The linear pressure drop profile is given as  $P_i = P_1 - i(P_1 - P_{NT+2}) / NT$  where  $P_i$  is the pressure in  $i^{\text{th}}$  tray,  $P_1$ , the pressure in the reboiler and  $P_{NT+2}$ , the pressure in the reflux drum.

### 4. MODELS FOR VAPOR-LIQUID EQUILIBRIUM

In modeling of batch distillation column, the selection of proper thermodynamic model affects the estimation of compositions highly and therefore is very crucial. In simulation studies, four different models are used for phase equilibrium and these models are explained below in detail.

#### 4.1 Model-I: Phase Equilibrium Using VLE data in Literature

VLE data for EtAc-EtOH-H<sub>2</sub>O-AcAc system given in Table 2 is taken from literature (Suzuki et al., 1971). This data is utilized in the simulation as a preliminary check.

**Table 2. Vapor Liquid Equilibrium Data.**

EtAc	$\log K = -2.3 \times 10^3/T + 6.742$
EtOH	$\log K = -2.3 \times 10^3/T + 6.588$
H <sub>2</sub> O	$\log K = -2.3 \times 10^3/T + 6.484$
AcAc	$K = (2.25 \times 10^{-2})/T - 7.812$ for $T > 347.6$ K $K = 0.001$ for $T \leq 347.6$ K

#### 4.2 Model-II: Phase Equilibrium Using $\phi - \phi$ Approach

In this approach, Peng Robinson EOS (PR) with van der Waals one-fluid mixing rule is used to calculate the fugacity of species for both liquid and vapor phases. The binary interaction parameters are given in Table 3 (Burgos-Solorzano, 2004).

**Table 3. Binary interaction parameters,  $k_{ij}$ .**

$k_{ij}$	EtAc	EtOH	H <sub>2</sub> O	AcAc
EtAc	0.0	0.022	-0.280	-0.226
EtOH	0.022	0.0	-0.935	-0.0436
H <sub>2</sub> O	-0.280	-0.935	0.0	-0.144
AcAc	-0.226	-0.0436	-0.144	0.0

#### 4.3 Model-III: Phase Equilibrium Using Combination of EOS with Excess Free Energy Models (EOS- $G_{ex}$ Approach)

In this method, activity coefficient models are incorporated into EOS. NRTL, Wilson, and UNIQUAC models are used

and performances for the system under consideration are compared. The parameters for these models are obtained from Tang et al. (2003), Okur and Bayramoğlu (2001), and Kang et al., (1992).

In this study, as EOS; PR and Peng-Robinson-Stryjek-Vera (PRSV) (Stryjek and Vera, 1986) are used.  $\kappa_1$  parameters for components are given in Table 4 (Stryjek and Vera, 1986). As the mixing rule, van der Waals one-fluid mixing rule, Huron-Vidal (Original) Mixing Rule (HVO), and Orbey-Sandler modification of the Huron-Vidal mixing rule (HVOS) are used.

**Table 4. PRSV EOS parameters,  $\kappa_1$  .**

Components	$\kappa_1$
EtAc	0.0693
EtOH	-0.03374
H <sub>2</sub> O	-0.06635
AcAc	-0.19724

4.4 Model-IV: Phase Equilibrium Using  $\gamma-\phi$  Approach

In VLE descriptions with the  $\gamma-\phi$  approach, an activity coefficient model can be used for the liquid phase and an EOS is used for the vapor phase.

5. RESULTS AND DISCUSSION

This study is done in three phases. In first phase, modeling studies are done and then checked with a simulation study found from the literature which has the same reactive system. In second phase, experimental studies are done and data is collected for total and different reflux ratios. In third phase, the experimental findings and the simulation results are compared and the dynamic model is finalized by selecting the appropriate thermodynamic model for VLE calculations.

The properties of the column which is used in simulation are given in Table 5. Monroy-Loperena and Alvarez-Ramirez (2000) used the VLE data of Model-I and temperature independent rate constants with  $k_1$  of  $4.76 \times 10^{-4}$  lt/(gmol.min) and  $k_2$  of  $1.63 \times 10^{-4}$  lt/(gmol.min). The comparison of dynamic model using same rate expression at total reflux is given in Fig. 2. As can be seen, the results are almost the same. This indicates that the developed dynamic model is quite satisfactory to represent this non-linear and complex problem of RBDC behaviour.

**Table 5. RBDC Specifications**

No. of stages (including reboiler and total condenser)	10
Total fresh feed, kmol	5.0
Feed composition (EtAc, EtOH, H <sub>2</sub> O, AcAc), mole fraction	0.0, 0.45, 0.1, 0.45
Column holdup, kmol	
condenser	0.1
internal plates	0.0125
Condenser vapor load, kmol/h	2.5
Column pressure, bar	1.013

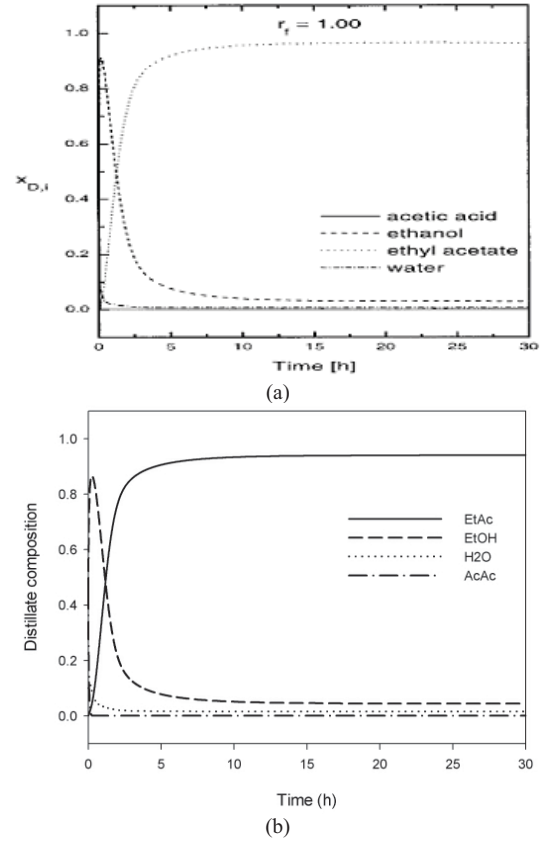


Fig. 2. Distillate compositions at total reflux. (a) Results from literature (b) Results from the simulation in this study.

After obtaining similar results with literature, experiments are performed in order to improve the model. Column is first operated at total reflux until the steady state is reached. Then it is operated with arbitrary reflux ratios and data for distillate and reboiler compositions are collected with respect to time.

5.1 Dynamic Analysis of the Results of Experimental and Simulation Studies

There is a difference in initialization of the experiments and simulation program. Therefore, although the trends of the profiles of compositions are similar, they cannot be compared up to steady state point. Consequently, if the two results match at total reflux steady state, then comparisons of dynamic response can be done. Thus, for each model explained in Section 4, the experimental data collected is checked with the simulation results.

Model-I: In Table 6, simulation result of Model-I and experiments at total reflux steady state are given. It can be seen that, when steady state values are compared, they are too different from each other and there is no need to check the dynamic behaviour. More accurate VLE model is needed.

**Table 6. Total Reflux Steady State Composition Values**

Comp.	Distillate		Reboiler	
	Exp.	Sim.	Exp.	Sim.
EtAc	0.5222	0.9384	0.1434	0.2582
EtOH	0.2408	0.0476	0.3189	0.1829
H <sub>2</sub> O	0.2371	0.0135	0.1918	0.3684
AcAc	0.0000	$5.61 \times 10^{-4}$	0.3459	0.1906

*Model-II:* The results of simulation that uses Model-II and experiments are given in Fig. 3. It is found that total reflux steady state values are better compared to Model-I. The comparison is further continued dynamically for a constant reflux ratio of 5.72. The time at total reflux steady state is shown as zero. It can be seen that there are great differences in the distillate and reboiler liquid composition trends with respect to time.

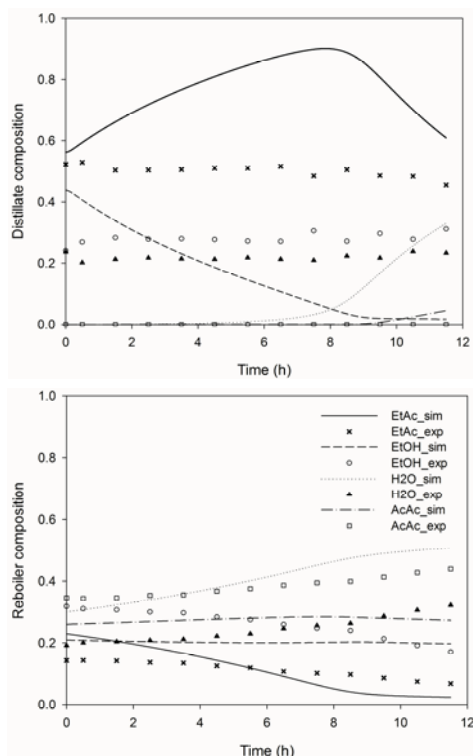


Fig. 3. Results with Model-II

*Model-III:* In Model-III, first of all PR with HVO mixing rule and NRTL activity coefficient model (Model-III-A) is tested. It can be seen from Fig. 4 that the results are somewhat improved compared to Model-II, especially for the reboiler compositions. However, the results for distillate compositions are not satisfactory. Therefore, EOS is changed to PRSV with same mixing rule and activity coefficient model; the performance of the system with this model (Model-III-B) is given in Fig. 5. Distillate compositions are much better than that of Model-III-A. However, reboiler compositions become worse and therefore this result is also found to be not satisfactory. As a further step, mixing rule is changed to HVOS and it is used together with PRSV and NRTL activity coefficient model (Model-III-C). The results are given in Fig. 6. The results for both distillate and reboiler compositions are improved significantly with this thermodynamic model.

In order to see the effects of different activity coefficient models, Wilson and UNIQUAC models are used in EOS- $G_{ex}$  approach. The distillate and reboiler liquid compositions with Wilson model (Model-III-D) and UNIQUAC model (Model-III-E) are given in Fig. 7 and Fig. 8, respectively. It can be seen from the figures that, while NRTL and Wilson models give similar results, UNIQUAC performs poorly. NRTL model is selected to be the most proper activity coefficient

model for this system, since it gives slightly better results than Wilson model, and will be used also in Model-IV.

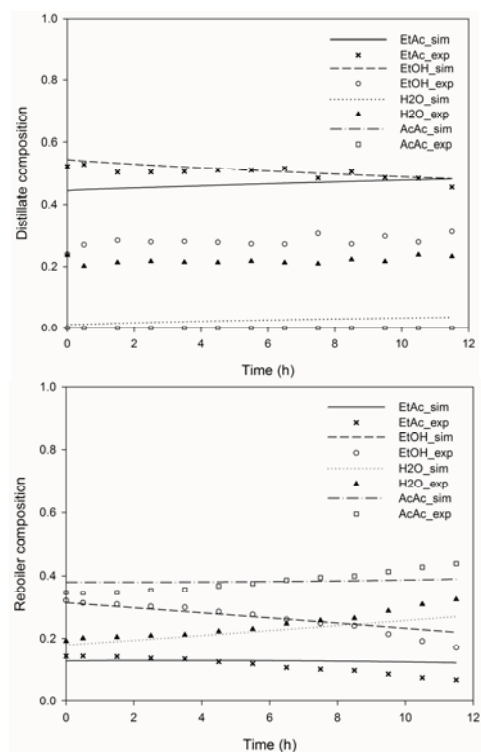


Fig. 4. Results with Model-III-A

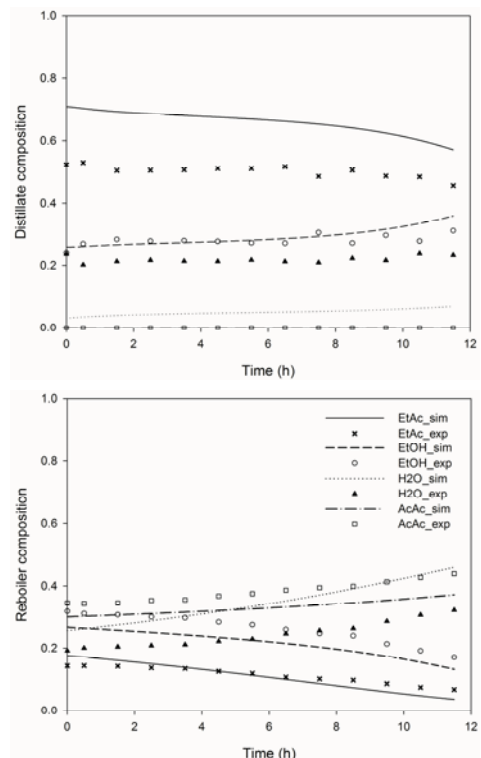


Fig. 5. Results with Model-III-B

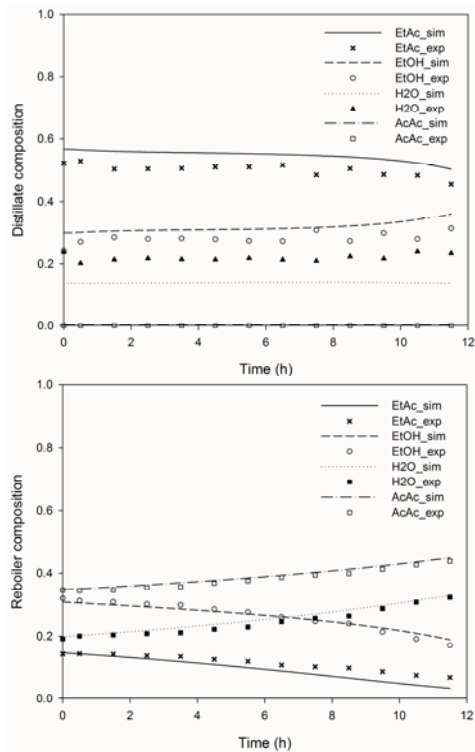


Fig. 6. Results with Model-III-C

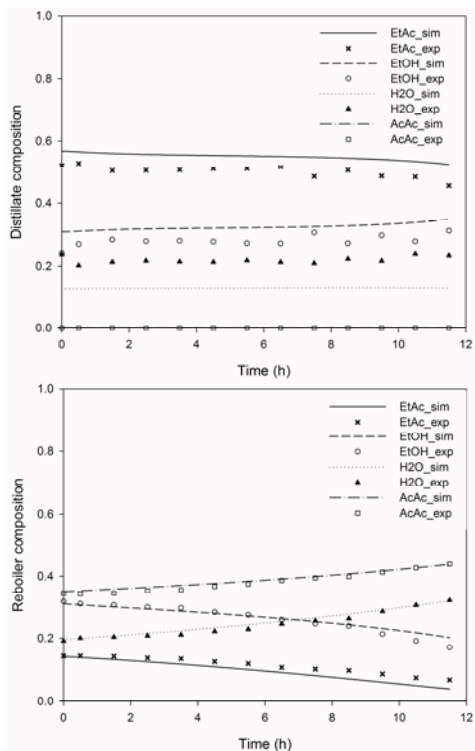


Fig. 7. Results with Model-III-D

an acceptable range. Unlike Model-III, PR also gives similar results with PRSV in Model-IV as can be seen in Fig. 10.

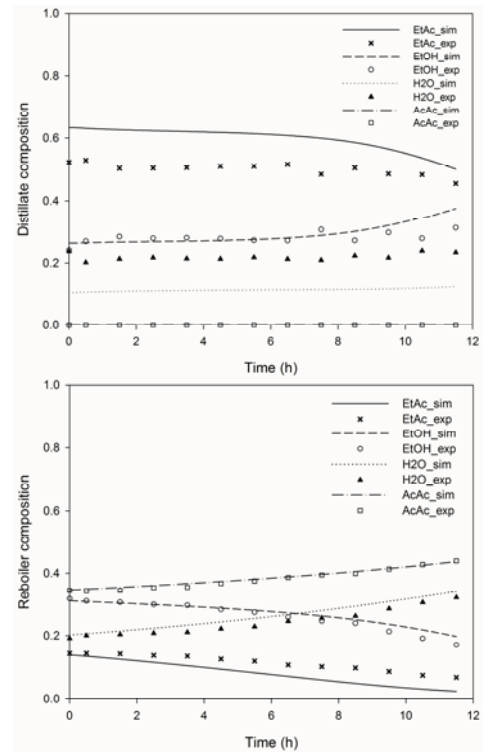


Fig. 8. Results with Model-III-E

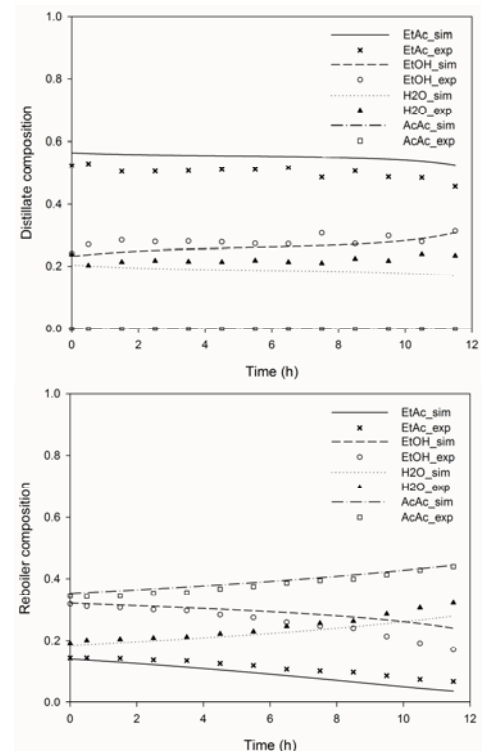


Fig. 9. Results with Model-IV-A

*Model-IV:* In Model-IV, NRTL activity coefficient model is used for liquid phase, PRSV (Model-IV-A) and PR (Model-IV-B) with van der Waals mixing rule is used for vapor phase. It can be seen from Fig. 9 that the distillate compositions are improved compared to Model-III. Although the reboiler compositions become a little worse, they are in

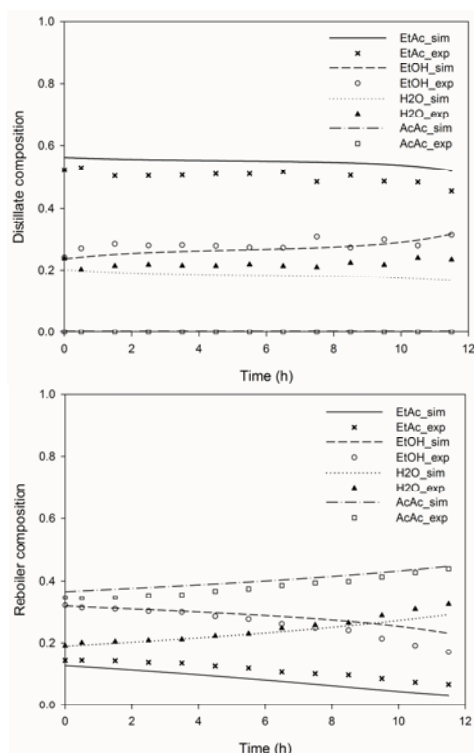


Fig. 10. Results with Model-IV-B

Table 7. Summary of Thermodynamic Models.

Model	Description	IAE Scores		
		Distillate	Reboiler	Overall
Model-I	VLE data from literature	-	-	-
Model-II	$\phi-\phi$ method (PR+van der Waals)	-	-	-
Model-III-A	EOS-G <sup>ex</sup> method (PR + HVO + NRTL)	6.080	1.049	7.129
Model-III-B	EOS-G <sup>ex</sup> method (PRSV + HVO + NRTL)	4.514	2.805	7.320
Model-III-C	EOS-G <sup>ex</sup> method (PRSV+HVOS+NRTL)	2.131	0.621	2.751
Model-III-D	EOS-G <sup>ex</sup> method (PRSV+HVOS+Wilson)	2.437	0.552	2.989
Model-III-E	EOS-G <sup>ex</sup> method (PRSV+HVOS+UNIQUAC)	2.915	0.877	3.791
Model-IV-A	$\gamma-\phi$ method (PRSV+van der Waals+NRTL)	1.321	1.026	2.347
Model-IV-B	$\gamma-\phi$ method (PR+van der Waals+NRTL)	1.279	1.072	2.351

## 6. CONCLUSIONS

A summary of results for different thermodynamic models are given in Table 7 with Integral Absolute Error (IAE) scores of response curves. Model-IV-A, which uses traditional  $\gamma-\phi$  approach with NRTL activity coefficient model for liquid phase and PRSV for vapor phase gives the smallest IAE score for the quaternary EtOH-AcAc-EtAc-H<sub>2</sub>O system. Nevertheless, Model-IV-B which uses the traditional approach with NRTL activity coefficient model for the liquid phase and the PR-EOS for the vapor phase, which is simple to use also gives similar result with a slightly higher IAE

score. Thus, both methods are suggested to be used in the simulation of EtOH esterification reaction with AcAc in a RBDC system.

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